Ontario

Determination of 1,6-Hexamethylene Diisocyanate (HDI) Emissions from Spray Booth Operations

Joint Ministry/Industry Study

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Ontario Ministry of the Environment

Acknowledgement

Acknowledgement and thanks is given for the hard work and participation in this study of the following:

AMEC Earth & Environmental Limited

Bayer Material Science's Environmental Analytics Group

BASF

DuPont Canada Inc.

Ventra Plastics

Committee Members

Executive Summary

In cooperation with the suppliers and users of isocyanates, the Ontario Ministry of the Environment (MOE) initiated a study of 1,6-Hexamethylene Diisocyanate (HDI) emissions with a focus on spray booth operations in the automotive industry. The primary objective of the study was to develop reliable emission factors for spray booth operations. The study had three (3) distinct phases. These included the development of the experimental design, then the on site measurement and analytical work which was followed by an evaluation of the test results and development of emission factors.

A stakeholder coordinating committee was established with a terms of reference. The committee as a whole developed the experimental design. The objective of the experimental design was to develop testing scenarios that would mimic actual operating practices in the auto body and original equipment manufacturing sectors. Committee member Bayer Material Science's Environmental Analytics Group performed the site measurement and analytical work at committee members BASF, DuPont Canada Inc. and Ventra Plastics facilities. The Ontario Ministry of the Environment (MOE) Standards Development Branch, Technology Standards Section, witnessed the testing. The MOE also retained AMEC Earth and Environmental (AMEC) to act as the Peer Reviewer for the study as well as to provide comment on the emission factors developed.

Emission factors have been developed for three (3) operating conditions as outlined in the table below. Due to the limited number of tests performed during the study and the number of physical factors that could affect the emissions no definitive conclusions can be made on the effect on HDI emissions by the following:

- Quality of filters;
- Age of filters;
- Size of paint job and;
- Transfer efficiency of the painting process.

Table 1: Summary of HDI Emission Factors and Ratings

Operating Conditions[2]	HDI Monomer Emission Factor [4] CAS # 822-06-0	HDI Polyisocyanate Emission Factor [1] CAS # 28182-81-2	Emission Factor Ratings[3]
Autobody Sector using Best Management Practices	**76**	**48**	**C**
Autobody Sector using Historical Practices	**81**	**63**	**C**
Original Equipment Manufacturer Sector	**35**	**18**	**D**

Table Notes:

(1) **HDI Polyisocyanate CAS # 28182-81-2 also includes:**

- HDI Biuret CAS # 4035-89-6
- HDI Isocyanurate CAS # 3779-63-3

(2) **Operating Conditions Definitions**

Autobody Sector using best management practices:

- Dry Filter Paint Booth (down draft or cross draft booths)
- High Efficiency Type Paint Spray System means equipment used for the application of automotive refinish coatings conforming to Section 3.4 *Application Equipment* of the Canadian Council of Ministers of the Environment (CCME) Guideline; “CCME Guideline” means the document entitled “National Standards and Guidelines for the Reduction of Volatile Organic Compounds from Canadian Commercial/Industrial Surface Coating Operations-Automotive Refinishing, October 1998, PN 1278", as amended, and published by CCME;
- Approved Automotive Refinish Coatings means automotive refinish coatings that comply with the VOC content limits indicated in Section 3.2.1 *VOC Content Limits* of the National Standards; “National Standards” means the document entitled “National Standards for the Volatile Organic Compound Content of Canadian Commercial/Industrial Surface Coating Products Automotive Refinishing, October 1998, PN 1288" and published by the CCME;

Autobody Sector using historical practices:

- Dry Filter Paint Booth (down draft or cross draft booths)
- Old style Conventional Spray Systems
- Unspecified Refinish Coatings

Original Equipment Manufacturer Sector:

- Water Wash Paint Booth

- Electrostatic Type Paint Spray System

(3) Emission Factor Ratings Definitions

Ratings based on US EPA document “Procedure for Preparing Emission Factor Documents: EPA-454/R-95-015, November 1997”.

C = Average. Emission factor is developed primarily from A, B and C rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.

D = Below Average. Emission factor is developed primarily from A, B and C rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population.

(4) Limitations of Emission Factors

As mentioned above due to the limited nature of the study general emission factors have been developed for the three (3) operating conditions. The limited data of the study does not allow for any “customization” of the emission factors (i.e. accounting for differences in paint transfer efficiencies between the test condition and emission factor users facility).

Auto body sector facilities with water wash paint booths should not use the emission factors derived for the original equipment manufacturer sector water wash booth as the operating conditions for the two types of facilities are very different. As no testing was performed on auto body sector water wash booths it is recommended that auto body facilities with water wash booths use the auto body sector dry filter emission factors according to the paint and spray systems used.

Most MSDS provide a range of potential concentrations for isocyanates in each specific paint component and most regulators would require the highest potential concentration to be used to calculate emission estimates suing these emission factors. However, it may be possible to obtain actual concentrations from paint manufacturers, enabling the user to reduce the resulting emission estimate, while also improving its accuracy.

Table of Contents

1.0 INTRODUCTION 1

2.0 BACKGROUND 2

2.1 Physical and Chemical Characteristics 2
2.2 Applications of Isocyanates in Surface-Coating Operations 3
2.3 Toxicology of HDI 4
2.4 Other Studies on Isocyanate Air Emissions 4

3.0 TEST PROTOCOL & EXPERIMENTAL DESIGN 5

3.1 Test Protocol 5
3.2 Experimental Design 6
3.2.1 Auto body Sector 7
3.2.2 Original Equipment Manufacturers Sector 8

4.0 TEST RESULTS 10

4.1 Auto Body Sector: Dry Filter Spray Booth Results 10
4.2 Original Equipment Manufacturers Sector: Water Wash Spray Booth Results 13

5.0 DEVELOPMENT OF EMISSION FACTORS 15

5.1 Auto Body Sector using Best Management Practices Emission Factor 17
5.2 Auto Body Sector using Historical Practices Emission Factor 17
5.3 Original Equipment Manufacturer Sector Emission Factor 17

6.0 PEER REVIEW 18

6.1 Experimental Design Observations 18
6.2 Source Testing Observations 19
6.3 Uncertainty Analysis for Test Results 19
6.4 Data Quality & Emission Factor Rating 20

7.0 CONCLUSIONS 20

8.0 RECOMMENDATIONS 22

List of Tables:

Table 1: Summary of HDI Emission Factors and Ratings ii
Table 2: Chemical Properties of HDI 2
Table 3: Isocyanate Compounds for which this Test Method is Applicable 6
Table 4: Summary of Test Scenarios 9
Table 5: SUMMARY of HDI EMISSIONS from DRY FILTER BOOTHS 12
Table 6: Dry Filter Booth Particle Size Distribution by Test Scenario 13
Table 7: Summary of HDI Emissions from Water Wash Booth 14
Table 8: Water Wash Booth Particulate Size Distribution 15
Table 9: HDI Emission Factors for Automotive Spray Applications (Units: grams HDI emitted/kilogram HDI sprayed) 15
Table 10: General Uncertainty of HDI Concentrations 20
Table 11: Summary of HDI Emission Factors and Ratings (units: g HDI emitted/kg HDI sprayed) 21

List of Figures:

Figure 1: Automotive Coating Application 4
Figure 2: Sampling Train 5
Figure 3: View of the stack when the sampling trains were being removed from the stack. 10
Figure 4: View of the paint booth used with the car body inside. 11
Figure 5: Filter sample recovery 14

Appendices

Appendix A **Study Terms of Reference & List of Study Group Members**

Appendix B **List of Reference Technical Documents**

Appendix C **Experimental Test Method**

- Sample Collection
- Method Approval
- Analysis Method

Appendix D **Experimental Design**

Appendix E **Material Safety Data Sheets for Paint Products & Spray Gun Specifications**

Appendix F **Test Result Reports**

- Determination of 1,6-Hexamethylene Diisocyanate (HDI) Emissions from Spray booth Operations (Conditional Test Method 036) at DuPont Canada Inc. and BASF
- Determination of 1,6-Hexamethylene Diisocyanate (HDI) Emissions from Spray booth Operations (Conditional Test Method 036) at Ventra Plastics

Appendix G **Emission Calculations**

Appendix H **Ministry Witnessing Reports**

- Source Testing Witnessing Report BASF Canada Inc.
- Source Testing Witnessing Report DuPont Canada Inc.

Appendix I **Peer Review Report**

- Peer Review Determination of 1,6-Hexamethylene Diisocyanate (HDI) Emissions From Multiple Spray Booth Operations

1.0 INTRODUCTION

In cooperation with the suppliers and users of isocyanates, the Ontario Ministry of the Environment (MOE) initiated a study of 1,6-Hexamethylene Diisocyanate (HDI) emissions with a focus on spray booth operations in the automotive industry. The primary objective of the study was to develop reliable emission factors for spray booth operations. The study had three (3) distinct phases. These included the development of the experimental design, then the on site measurement and analytical work which was followed by an evaluation of the test results and development of emission factors.

A stakeholder coordinating committee was established with a terms of reference. Please see Appendix A for a list of the committee members and the full terms of reference. The deliverables outlined in the terms of reference are as follows:

Experimental Design

Development of an experimental design plan that outlines the details and scope of the Isocyanates Air Emissions Study.

Report of the Results of the Isocyanates Air Emissions Study

The report will include:

- Background material on isocyanates including:
    - physical and chemical characteristics;
    - production and uses of various isocyanates in surface-coating operations;
    - toxicological information; and
    - any information from other isocyanate air emission studies or reports with suggested approaches to estimating isocyanate air emissions;
- Description of the test protocols used in the study to measure isocyanate compounds in air;
- Description of the experimental design, process sources and operating conditions during the testing for isocyanates;
- Results of the air emission testing for isocyanates;
- Development and documentation of isocyanate emission factors (i.e., mass of isocyanate emitted per unit production or material usage);
- Identification of the assumptions and limitations of the study; and

- Recommendations for future activities or improvement to the understanding of how isocyanates are emitted.

The committee as a whole developed the experimental design. Committee member Bayer Material Science's Environmental Analytics Group performed the on site measurement and analytical work at committee members BASF, DuPont Canada Inc. and Ventra Plastics facilities. The Ontario Ministry of the Environment (MOE) Standards Development Branch, Technology Standards Section, witnessed the testing. The MOE also retained AMEC Earth and Environmental (AMEC) to act as the Peer Reviewer for the study as well as to provide comment on the emission factors developed.

2.0 BACKGROUND

2.1 Physical and Chemical Characteristics

The HDI monomer is an aliphatic diisocyanate that exists as a combustible, colourless to clear liquid. It has an irritating, sharp, pungent odour, with an odour threshold of 0.001 ppm (0.007 mg/m3). The HDI monomer is readily soluble in organic solvents. In the manufacturing of commercial HDI products, the monomer is allowed to polymerize into either of two (2) polyisocyanates: HDI biuret (HDI-BT) or HDI isocyanurate (HDI-IC). Industry often refers to HDI-BT and HDI-IC jointly as HDI polyisocyanates [CAS # 28182-81-2]. Because of their very low vapour pressure they will be present in the atmosphere only in a mist or aerosol form. The following list provides some specific information on HDI and its properties (Ref: MOE 2004):

Table 2: Chemical Properties of HDI

Property	HDI monomer	HDI Biuret Polyisocyanate	HDI Isocyanurate Polyisocyanate
CAS #	822-06-0	4035-89-6 28182-81-2	3779-63-3 28182-81-2
RTECS #	MO1740000	NQ9170000	NQ9170000
UN #	UN2281	NA3082	Not applicable
Conversion factors	1 ppm = 6.9 mg/m^3 1 mg/m^3 = 0.14 ppm	Not applicable	Not applicable
Melting Point	-67 to -55 °C	-23 °C	-24 °C
Boiling Point	213 – 255 °C	Not measurable; decomposes	Not measurable; decomposes

Property	HDI monomer	HDI Biuret Polyisocyanate	HDI Isocyanurate Polyisocyanate
Flash Point	130 – 135 °C	166 – 191 °C*	158 – 238 °C*
Water Solubility	Not soluble, reacts with water	Not soluble, reacts with water	Not soluble, reacts with water
Log Kow	Not established	Not established	Not established
Formula	$C_8H_{12}N_2O_2$	Not applicable	Not applicable
Molecular Weight	168	Approx. 500	Approx. 500
Specific Gravity (water = 1)	1.05 @ 25 °C	1.14 @ 20 °C* 1.11-1.113 @ 25 °C*	1.16 @ 20 °C* 1.12 @ 25 °C*
Vapour Density (air = 1)	5.8 – 6	Not applicable	Not applicable
Vapour Pressure	<0.01 mm Hg @ 20°C 0.011 mm Hg @ 25°C	0.00000047 mm Hg @ 20 °C	0.0000000052 mm Hg @ 20 °C
Synonyms	1,6-Hexamethylene diisocyanate; 1,6-Diisocyanatohexane	HDI homopolymer; HDI-BT	HDI homopolymer; HDI-IC

This table summarizes the chemical properties of HDI monomer; HDI Biuret Polyisocyanate; and HDI Isocyanurate Polyisocyanate.

Table Note:

*** The different values may reflect differences in the conditions at which the test was conducted, differences in the test methodology, or differences in the specific composition of the homopolymer tested.**

2.2 Applications of Isocyanates in Surface-Coating Operations

1, 6-Hexamethylene diisocyanate monomer is primarily used as a chemical intermediate in the manufacture of higher molecular weight polyisocyanates (both biuret and isocyanurate types). These products are used as curing agents in foams and polyurethane paint for cars, marine coatings, industrial maintenance and other high performance coatings (Ref: MOE 2004).

1, 6-Hexamethylene diisocyanate is used in a variety of surface-coating systems in the automotive industry. Applications range from use as hardeners to a catalyst component of paints used in auto-body shops, and some auto-parts painters.

Figure 1: Automotive Coating Application

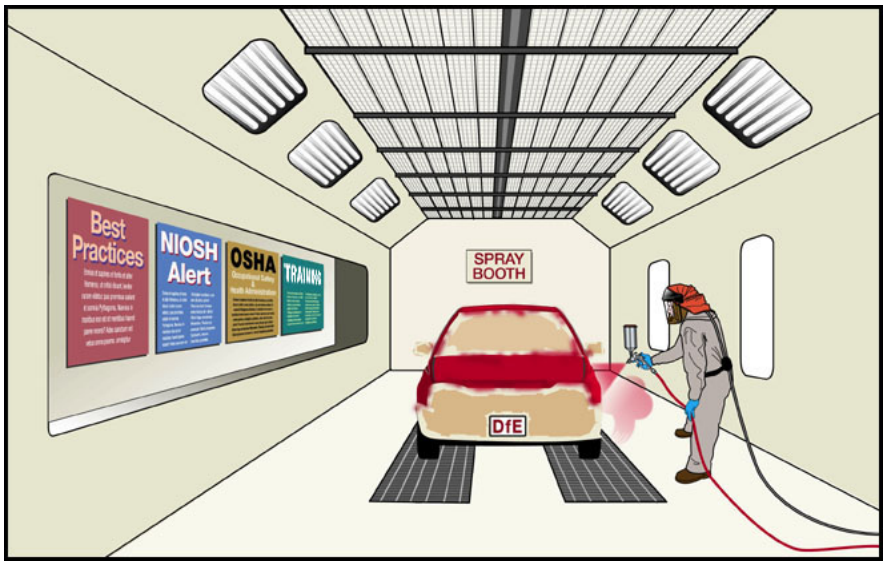

Figure 1 is a picture depicting a spray booth in operation

2.3 Toxicology of HDI

Exposures resulting from inhalation or dermal contact are the most probable routes of human exposure to HDI. HDI is an extreme eye, nose, throat and lung irritant and can result in respiratory sensitization (Ref: MOE 2004). For more information on the toxicological effects of HDI please refer to the Rationale for Development of Ontario Air Standards for Hexamethylene Diisocyanate (HDI) Monomer and Polyisocyanates document prepared by the MOE.

2.4 Other Studies on Isocyanate Air Emissions

Isocyanates have a relatively low volatility and high reactivity so that only a small but poorly defined fraction is emitted to atmosphere. There is presently only a small amount of technical information with respect to isocyanate air emissions. Appendix B contains a list of technical reports referenced during this study. As a result of this limited information it is difficult to develop appropriate estimates of emission rates and impacts. Before this study, MOE accepted estimating practices that used a mass balance approach assuming 100% of the 1, 6-Hexamethylene Diisocyanate (HDI) monomer and 1% of the HDI polyisocyanate is emitted to atmosphere. However, recent information presented in a Bayer Corporation report (Bayer 1999) suggested that this approach over-estimates the monomer emission rates and under-estimates the polyisocyanate emission rates. In the past, the use of a monomer component of isocyanates was relatively common. However, recently monomer contents have been reduced and a polyisocyanate component of isocyanates has become more common. With this change in monomer and polyisocyanate concentrations in the paint mixtures, along with the low volatility

and high reactivity of isocyanates, there is a fair amount of uncertainty regarding the actual isocyanate emissions.

3.0 TEST PROTOCOL & EXPERIMENTAL DESIGN

3.1 Test Protocol

The MOE retained Bayer Material Science LLC (Bayer) to develop a test method for determining 1,6-Hexamethylene Diisocyanate (HDI) emissions from spray booth operations. This method was developed and submitted to the United States Environmental Protection Agency (US EPA) for approval as a valid sampling and analytical method as per the requirements of US EPA Method 301. Method 301 describes procedures for determining and documenting the quality, i.e., systematic error (bias) and random error (precision), of the measured concentrations from an affected source. On March 10th, 2004 Bayer received a letter of acceptance of the Method 301 Validation Report submitted for the HDI test method. The method was designated as Conditional Test Method 036 (CTM-036). A copy of the sample collection method, method approval letter and analysis method is included in Appendix C.

Summary of Method

Under Conditional Test Method 036, gaseous and/or aerosolized isocyanates are withdrawn from an emission source at an isokinetic sampling rate and are collected on a 90 mm glass fiber filter coated with 10-12 µg/mm^2 of 1-(2-pyridyl)piperazine (1,2-PP) or 1-(2-methoxyphenyl)piperazine (1,2-MP). The primary components of the train include a filter cassette, and a sampling pump. The collected samples are then analyzed by high performance liquid chromatography (HPLC).

Figure 2: Sampling Train

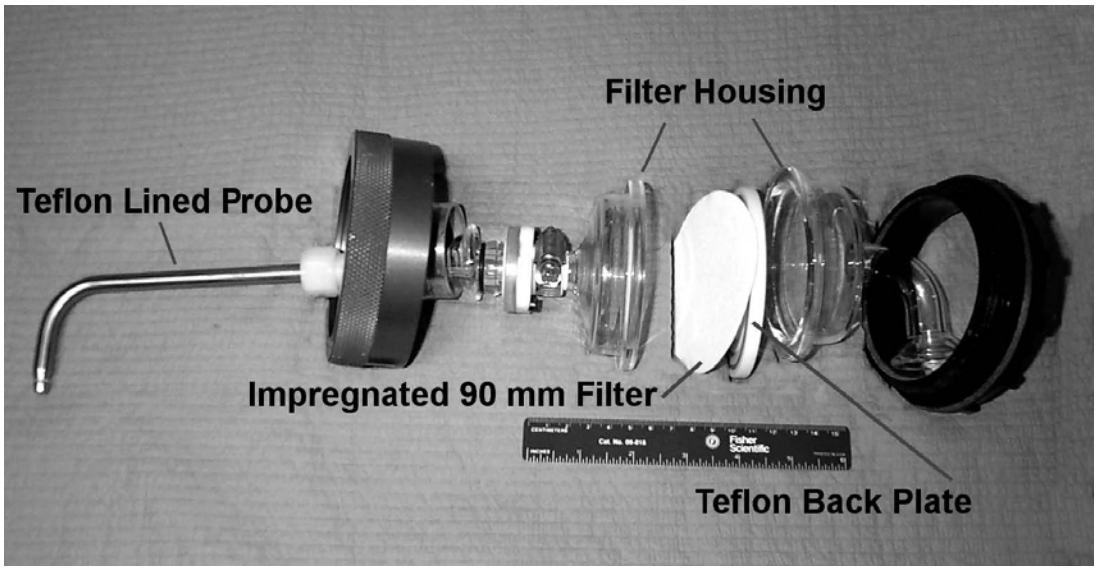

Figure 2 above is a picture of a Sampling Train with a ruler to indicate actual size

This method is applicable to the collection of Toluene Diisocyanate (TDI), Methylenediphenyl Diisocyanate (MDI), Hexamethylene Diisocyanate (HDI), HDI Biuret, HDI Trimer, and isophorone diisocyanate (IPDI).

Table 3: Isocyanate Compounds for which this Test Method is Applicable

Compound Name	CAS No.	Detection Limits $(\mu g/M3)_a$
1,6-Hexamethylene Diisocyanate (HDI)	822-06-0	0.043
1,6-Hexamethylene Diisocyanate Biuret [b]	4035-89-6 28182-81-2	0.48
1,6-Hexamethylene Diisocyanate Trimer [c]	3779-63-3 28182-81-2	0.30
Isophorone Diisocyanate (IPDI)	4098-71-9	0.27
2,4-Toluene Diisocyanate (TDI)	584-84-9	0.18
2,6-Toluene Diisocyanate (TDI)	91-08-7	0.036
2,4'-Methylenediphenyl Diisocyanate	5873-54-1	0.64
4,4'-Methylenediphenyl Diisocyanate	101-68-8	0.64

Table Notes:

[a] Estimated method detection limit is based on a sample volume of 0.25 M^3 and a 5 mL sample extraction volume

[b] N,N'-2-Tris(6-isocyanatohexyl)imidodicarbonic diamide.

[c] 1,3,5-Tris(6-isocyanatohexyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione; HDI isocyanurate.

3.2 Experimental Design

For the purposes of the study, an experimental design was developed through consultation with the stakeholders committee, consisting of representatives from the MOE, as well as the automotive and coating sectors. The objective of the experimental design was to develop testing scenarios that would mimic actual operating practices in the auto body and original equipment manufacturing sectors. Scenarios were developed to represent the following practices:

3.2.1 Auto body Sector

Operating Condition A – typical operating practices at an approved auto body facility using best management practices:

- Use of High Volume Low Pressure (HVLP) spray guns;
- Use of high solids paint; and
- Use of manufacturer specified paint booth filters in down draft or cross draft paint booths.

Operating Condition B - typical historical operating practices at an auto body facility:

- Use of conventional spray guns; and
- Use of low solids paint

Other variables were also incorporated into the experimental design as follows:

- Quality of filters (i.e. manufacturer specified filters versus poorer quality filter);
- Age of filter (i.e. new filter versus filter which has been in use);
- Size of Paint Job (painting of whole car versus painting of part); and
- Transfer Efficiency of the paint from the spray gun onto the painted surface.

This test design translated into twelve (12) different test scenarios divided between two (2) different facilities and three (3) separate paint booths. Three (3) runs would be performed for each test scenario with duplicate samples taken for each run. Table 4 below summarizes the test program as set in the experimental design.

DuPont Canada Inc. supplied the paint to be used during the dry filter spray booth testing.

For the purpose of this study it was determined that the high solid coating used at the DuPont and BASF facilities would be ChromaClear 7900S a two (2) component clear coat produced by DuPont. The clear coat is made up of ChromaClear 7900S mixed with Dupont's ChromaClear fast activator/reducer 7975S at a 3 parts of coat for 1 part of activator mix ratio. The 7975S contains 0.12% HDI monomer and 57.61% HDI polyisocyanate. This results in a total paint HDI monomer and HDI polyisocyanate concentration of 0.031 wt % and 15.3 wt % respectively. This product is a relatively quick dry and optimum appearance clear coat designed to meet US EPA low Volatile Organic Compound (VOC) content (base/clear average VOC content of 5.0 lb/gal (0.60 kg/L)) regulations. DuPont has five (5) other clear coats all containing in the same range of VOC and 1,6-hexamethylene diisocyanate content. DuPont believes this product is indicative of the general products on the market.

The low solid paint used for the low solid scenario at the DuPont facility was a three part DuPont ChromaClear product. The 7500S/7525S/7570S ratio of paint/activator/solvent is 8/2/1. The

7525S contains 0.126 wt% HDI monomer and 62.96 wt% HDI polyisocyanate. This results in a total paint HDI monomer and HDI polyisocyanate concentration of 0.025 wt% and 12.6 wt% respectively. This product was designed in the mid-eighties and was the highest sales volume clear coat prior to the US EPA VOC regulations (base/clear average VOC content of 0.67 kg/L (5.5 lb/gal). This product is still sold to non-VOC regulated shops as "cheap" clear coat. According to DuPont most generic low solids clear coats are within five (5) percent of the concentrations of HDI and VOC in this clear coat.

Appendix E contains the Material Safety Data Sheets (MSDS) for both of these paints.

3.2.2 Original Equipment Manufacturers Sector

Operating Condition C – typical operating practices at an auto assemble or parts painting facility using the following practices:

- Water wash paint booth;
- Robotic spray applications;
- Electrostatic paint spray system.

This test design translated into two (2) different test scenarios performed at one facility. The two (2) scenarios differed only in the length of time of the sampling as all other variables in the process are dictated by the facility's client specified production standards. Three (3) runs would be performed for each test scenario with duplicate samples taken for each run. Table 4 below summarizes the test program as set in the experimental design.

The clear coat used at the Ventra facility is a two (2) part Rohm and Hass product with the ratio of 3.4 parts 2K Clear and 1 part catalyst. The catalyst contained 0.1% HDI monomer and 64.9% HDI polyisocyanate. Appendix E contains the MSDS sheets for this paint.

The percent HDI monomer and polyisocyanate given in the paint formulations above were obtained directly from the paint manufacturers. While the manufacturers can provide an accurate percentage typical MSDS sheets state a percentage range.

Table 4: Summary of Test Scenarios

DuPont Canada Inc., Ajax, Ontario, Canada -Down Draft Booth				
Test Scenario	**Coating Type**	**Gun Type**	**Spray Pressure**	**Operation Scenario**
Scenario 1	High Solid	Devilbiss GTI HVLP	9 PSI	Booth Contents: Car Filters: MRF*
Scenario 2	High Solid	Devilbiss GTI HVLP	14 PSI	Booth Contents: Car Filters: MRF
Scenario 3	High Solid	Conventional	50 PSI	Booth Contents: Car Filters: MRF
Scenario 4	Low Solid	Conventional	50 PSI	Booth Contents: Car Filters: MRF
Scenario 5	High Solid	Devilbiss GTI HVLP	9 PSI	Booth Contents: Empty Filters: MRF
Scenario 6	High Solid	Devilbiss GTI HVLP	9 PSI	Booth Contents: Car Filters: clean MRF
BASF, Toronto, Ontario, Canada -Down Draft Booth				
Test Scenario	**Coating Type**	**Gun Type**	**Spray Pressure**	**Operation Scenario Tested**
Scenario 1	High Solid	Devilbiss GTI HVLP	10 PSI	Booth Contents: Car Filters: MRF
Scenario 2	High Solid	SATA HVLP	10 PSI	Booth Contents: Car Filters: MRF
Scenario 3	High Solid	Devilbiss GTI HVLP	10 PSI	Booth Contents: Car (only 2 doors, rear quarter panel coated) Filters: MRF
Scenario 4	High Solid	Devilbiss GTI HVLP	10 PSI	Booth Contents: Empty Filters: MRF
Scenario 5	High Solid	Devilbiss GTI HVLP	10 PSI	Booth Contents: Car Filters: after-market filter
BASF, Toronto, Ontario, Canada -Semi Cross Draft Booth				
Test Scenario	**Coating Type**	**Gun Type**	**Spray Pressure**	**Operation Scenario Tested**
Scenario 1	High Solid	Devilbiss GTI HVLP	10 PSI	Booth Contents: Car Filters: MRF
Ventra Plastics, Peterborough, Ontario, Canada -Water Wash				
Test Scenario	**Coating Type**	**Gun Type**	**Spray Pressure**	**Operation Scenario Tested**
Scenario 1	High Solid	Electrostatic Conventional	-	Booth Contents: Car Parts 30 min sample period
Scenario 2	High Solid	Electrostatic Conventional	-	Booth Contents: Car Parts 10 min sample period

Table Note: * MRF = Manufacturer Recommended Filter

Appendix D includes the experimental design.

4.0 TEST RESULTS

The actual source testing phase of the study was conducted in June and August of 2004, in accordance with the test program outlined in Table 4 above.

4.1 Auto Body Sector: Dry Filter Spray Booth Results

Bayer Material Science's Environmental Analytics group (Bayer) conducted the testing at both dry filter spray booth locations. Bayer performed particulate size distribution sampling along with the testing protocol summarized in section 3.1 above. Appendix F contains Bayer's emission testing report. Tables 5 and 6 below summarize emission and particle size distribution results. Appendix G details how the emission results presented in Table 6 were calculated.

DuPont Facility

Testing at the DuPont facility in Ajax was performed over a three (3) day period from June 1st to 3rd, 2004. The facility is DuPont's training centre for its auto body clients. Painting applications during the testing was performed by a DuPont instructor at the facility who is an experienced painter. Specifications of the spray guns used during the testing can be found in Appendix E.

Six (6) scenarios were tested. AMEC personnel observed the sampling of scenarios 1 through 5, on June 1st and 2nd. MOE Standards Development Branch, Technology Standards Section, also witnessed the performance of Scenario 1 and the first test of Scenario 2. Scenario 6, performed on June 3rd, was not witnessed. A copy of MOE's witness report can be found in Appendix H. A copy of AMEC's peer review report can be found in Appendix I.

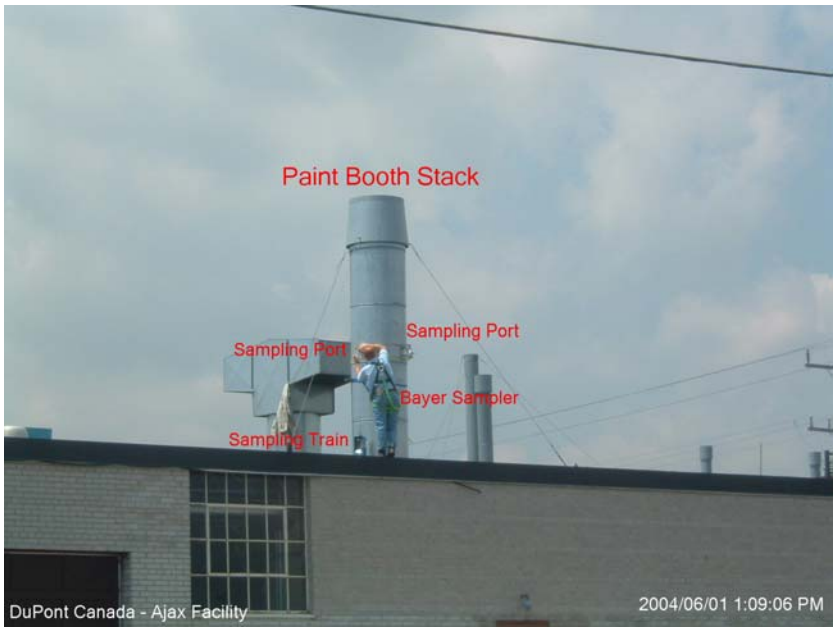

Figure 3: View of the stack when the sampling trains were being removed from the stack.

BASF Facility

Testing at the BASF facility in Toronto was performed over a three (3) day period from June 8th to 10th, 2004. The facility is BASF's training center for its auto body clients. Painting applications during the testing was performed by a BASF instructor at the facility who is an experienced painter. Specifications of the spray guns used during the testing can be found in Appendix E.

Six (6) scenarios were tested. AMEC personnel observed the sampling of all scenarios. MOE Standards Development Branch, Technology Standards Section, also witnessed test 2 and 3 of Scenario 2. A copy of MOE's witness report can be found in Appendix H. A copy of AMEC's peer review report can be found in Appendix I.

Figure 4: View of the paint booth used with the car body inside.

Table 5: SUMMARY of HDI EMISSIONS from DRY FILTER BOOTHS

Location	Amount of Paint Sprayed (kg)	Amount of HDI Sprayed (kg)		HDI Emissions Measured in Stack (g/s)		HDI Emissions as	
DuPont Canada, Inc Down Draft Booth		HDI Monomer	HDI Polyisocyanate	HDI Monomer	HDI Polyisocyanate	HDI Monomer	HDI Polyisocyanate
Scenario 1	1.65	5.1E-04	2.52E-01	1.34E-05	6.03E-03	47.1	43.1
Scenario 2	1.94	6.0E-04	2.96E-01	2.00E-05	9.19E-03	60.0	55.8
Scenario 3	1.84	5.7E-04	2.82E-01	2.54E-05	8.64E-03	80.1	55.1
Scenario 4	2.34	5.9E-04	2.89E-01	2.63E-05	1.04E-02	81.2	63.2
Scenario 5	1.65	5.1E-04	2.52E-01	3.13E-05	5.34E-03	110.5	38.2
Scenario 6	1.65	5.1E-04	2.52E-01	2.65E-05	7.39E-03	93.5	52.9
BASF	(Averaged over 3 runs) (kg)						
Scenario 1	2.39	7.4E-04	3.66E-01	3.24E-05	7.42E-03	92.2	42.6
Scenario 2	2.21	6.9E-04	3.39E-01	2.83E-05	6.59E-03	74.2	35.1
Scenario 3	0.36	1.1E-04	5.50E-02	5.35E-06	1.57E-03	87.5	51.3
Scenario 4	2.22	6.9E-04	3.40E-01	3.85E-05	5.22E-03	99.6	27.3
Scenario 5	2.08	6.5E-04	3.19E-01	2.53E-05	9.15E-03	70.2	51.7
BASF	(Averaged over 3 runs) (kg)						
Scenario 6	2.10	6.5E-04	3.21E-01	2.89E-05	8.54E-03	79.6	47.9

Table 6: Dry Filter Booth Particle Size Distribution by Test Scenario

DuPont Canada, Inc.											
Size[1]	**0.3µm**	**0.4µm**	**0.5µm**	**0.65µm**	**0.8µm**	**1.0µm**	**1.6µm**	**2.0µm**	**3.0µm**	**4.0µm**	**5.0µm**
Scenario 1	42.97%	20.69%	11.62%	7.53%	8.94%	4.39%	1.71%	1.86%	0.25%	0.03%	0.00%
Scenario 2	33.32%	24.18%	12.33%	8.74%	11.60%	4.42%	2.44%	2.56%	0.35%	0.04%	0.01%
Scenario 3	29.09%	25.78%	11.84%	9.05%	13.64%	4.10%	2.83%	3.16%	0.45%	0.06%	0.01%
Scenario 4	21.04%	27.89%	11.21%	10.02%	17.49%	4.08%	3.58%	4.08%	0.54%	0.05%	0.01%
Scenario 5	35.90%	24.15%	13.54%	8.33%	9.47%	4.55%	1.75%	1.95%	0.31%	0.04%	0.01%
Scenario 6	40.91%	21.54%	11.69%	7.68%	9.46%	4.39%	1.85%	2.09%	0.33%	0.04%	0.01%
BASF, Toronto, Ontario Canada											
Scenario 1	**Detector Saturated at 0.3 µm range**										
Scenario 2	43.71%	20.76%	10.89%	7.13%	8.88%	3.39%	2.50%	2.45%	0.25%	0.02%	0.00%
Scenario 3	44.18%	20.60%	10.71%	7.16%	9.01%	3.22%	2.49%	2.38%	0.22%	0.02%	0.00%

Table Note: [1]Particles =/>7.5 µm accounted for <0.000001%

4.2 Original Equipment Manufacturers Sector: Water Wash Spray Booth Results

Bayer conducted the testing at the water wash booth location. Appendix F contains Bayer's emission testing report. Tables 7 and 8 below summarize emission and particle size distribution results. Appendix G details how the emission results presented in Table 7 were calculated.

Ventra Plastics Facility

Testing at the Ventra Plastics facility in Peterborough, Ontario was performed on August 3rd, 2004. Ventra Plastics manufactures, paints and finishes plastic automotive parts. Manufactured parts include fascias, bumpers, rocker panels and various plastic body panel assemblies and components. The painting process line consists of washing of the plastic components and sequential application of adhesion promoter, a colour (base) coat and a top (clear) coat finish with a curing process for the painted parts in a cure oven. Testing was conducted on the last paint booth which applies the clear coat. The paint booth is equipped with electrostatic spray guns and a falling water curtain located below the parts being coated. Specifications of the spray guns used during the testing can be found in Appendix E. The booth is exhausted to the atmosphere by two (2) stacks.

Two (2) scenarios were tested, with the only variable in the scenarios being the length of time of sampling. AMEC personnel observed the sampling of all scenarios. A copy of AMEC's peer review report can be found in Appendix I.

Figure 5: Filter sample recovery

Table 7: Summary of HDI Emissions from Water Wash Booth

Set-up No.	Amount of Paint Sprayed (kg)	Amount HDI Sprayed (kg)		HDI Emissions Measured in Stack (g/s)		Measured HDI as g/kg Sprayed	
		Monomer	Polyisocyante	Monomer	Polyisocyante	Monomer	Polyisocyante
1A	39.83	4.68E-03	3.04	4.32E-05	2.77E-02	16.6	16.4
1B	22.35	2.63E-03	1.70	6.95E-05	1.72E-02	47.6	18.1
1C	50.18	5.90E-03	3.83	6.09E-05	2.90E-02	18.6	13.4
2A	8.90	1.05E-03	6.79E-01	8.39E-05	2.09E-02	48.1	18.5
2B	8.98	1.06E-03	6.84E-01	9.14E-05	2.92E-02	52.9	25.6
2C	13.85	1.63E-03	1.06	6.62E-05	2.82E-02	24.4	16.0

Table 8: Water Wash Booth Particulate Size Distribution

Ventra Plastics											
Size[1]	**0.3µm**	**0.4µm**	**0.5µm**	**0.65µm**	**0.8µm**	**1.0µm**	**1.6µm**	**2.0µm**	**3.0µm**	**4.0µm**	**5.0µm**
Left Stack	32.7%	25.1%	18.3%	8.8%	8.8%	3.1%	2.3%	0.8%	0.01%	2.0E-04%	1.0E-06%

Table Note: [1]Particles =/>7.5µm accounted for <0.0000004%

5.0 DEVELOPMENT OF EMISSION FACTORS

These emission factors were developed based on the mass of HDI emitted, as measured in the stack, in relation to the total mass of HDI sprayed. The emission factors are expressed as "grams of HDI emitted per kilograms of HDI sprayed". The resulting emission factors are presented in Table 9.

Table 9: HDI Emission Factors for Automotive Spray Applications (Units: grams HDI emitted/kilogram HDI sprayed)

Operating Scenario (1)	HDI Monomer Emission Factor	HDI Polyisocyanate Emission Factor
Auto Body Sector using Best Management Practices ➢ Dry Filter Paint Booth ➢ High Efficiency Type Paint Spray System ➢ Approved Automotive Refinish Coatings	47.1 DuPont Scenario 1 60.0 DuPont Scenario 2 93.5 DuPont Scenario 6 92.2 BASF Scenario 1 74.2 BASF Scenario 2 87.5 BASF Scenario 3 70.2 BASF Scenario 5 79.6 BASF Scenario 6 **76 g/kg Averaged**	43.1 DuPont Scenario 1 55.8 DuPont Scenario 2 52.9 DuPont Scenario 6 42.6 BASF Scenario 1 35.1 BASF Scenario 2 51.3 BASF Scenario 3 51.7 BASF Scenario 5 47.9 BASF Scenario 6 **48 g/kg Averaged**
Auto Body Sector using Historical Practices ➢ Dry Filter Paint Booth	**81 g/kg** DuPont Scenario 4	**63 g/kg** DuPont Scenario 4

➢ Old style Conventional Spray Systems ➢ Unspecified Refinish Coatings (Low Solids Paint)		
Original Equipment Manufacturer Sector ➢ Water Wash Booth ➢ Electrostatic Type Paint Spray System ➢ High Solids Paints	16.6 Ventra Scenario 1 Run 1 47.6 Ventra Scenario 1 Run 2 18.6 Ventra Scenario 1 Run 3 48.0 Ventra Scenario 2 Run 1 52.0 Ventra Scenario 2 Run 2 24.4 Ventra Scenario 2 Run 3 **35 g/kg Averaged**	16.4 Ventra Scenario 1 Run 1 18.1 Ventra Scenario 1 Run 2 13.4 Ventra Scenario 1 Run 3 18.5 Ventra Scenario 2 Run 1 25.6 Ventra Scenario 2 Run 2 16 Ventra Scenario 2 Run 3 **18 g/kg Averaged**

Table Notes:

(1) Operating Conditions Definitions

Autobody Sector using best management practices:

- Dry Filter Paint Booth (down draft or cross draft booths)
- High Efficiency Type Paint Spray System means equipment used for the application of automotive refinish coatings conforming to Section 3.4 *Application Equipment* of the Canadian Council of Ministers of the Environment (CCME) Guideline; “CCME Guideline” means the document entitled “National Standards and Guidelines for the Reduction of Volatile Organic Compounds from Canadian Commercial/Industrial Surface Coating Operations-Automotive Refinishing, October 1998, PN 1278", as amended, and published by the CCME;
- Approved Automotive Refinish Coatings means automotive refinish coatings that comply with the VOC content limits indicated in Section 3.2.1 *VOC Content Limits* of the National Standards; “National Standards” means the document entitled “National Standards for the Volatile Organic Compound Content of Canadian Commercial/Industrial Surface Coating Products Automotive Refinishing, October 1998, PN 1288" and published by the CCME;

Autobody Sector using historical practices:

- Dry Filter Paint Booth (down draft or cross draft booths);
- Old style Conventional Spray Systems;
- Unspecified Refinish Coatings.

Original Equipment Manufacturer Sector:

- Water Wash Paint Booth;
- Electrostatic Type Paint Spray System;
- High Solids Paints (base/clear average VOC content of 5.0 lb/gal (0.48 kg/L))

5.1 Auto Body Sector using Best Management Practices Emission Factor

The auto body sector using best management practices emission factor was derived from three (3) test scenarios performed at the DuPont facility and five (5) test scenarios performed at the BASF facility. These test scenarios while similar are not identical. All test scenarios used in this emission factor have the following in common:

- All use high efficiency type paint spray system;
- All use approved automotive refinish coatings (high solids paint);
- All are tested in a dry filter paint booth.

The slight variations are as follows:

- Painting job performed (i.e. full car versus parts);
- Quality and age of booth exhaust filters;
- Spray gun pressure and;
- Type of paint booth (i.e. down draft versus semi-cross draft booth).

The logic behind choosing these test scenarios was to base the emission factor on the largest data set possible as this operating condition is likely the most typically used in the auto body sector. The slight variation in the test scenarios also reflects the variations in this operating condition found in the sector. Due to these variations in test scenarios no statistical analysis was performed on the data.

5.2 Auto Body Sector using Historical Practices Emission Factor

The auto body sector using historical practices emission factor was derived from one (1) test scenario performed at the DuPont facility. Since the data set used for this emission factor is made up of three (3) test runs of this one test scenario no statistical analysis was performed on the data.

5.3 Original Equipment Manufacturer Sector Emission Factor

The original equipment manufacturer sector emission factor was derived from two (2) test scenarios performed at the Ventra facility. The data set used for this emission factor was made

up of three (3) test runs per each test scenario. Due to this limited data set no statistical analysis was performed on the data.

6.0 PEER REVIEW

The MOE retained AMEC to act as the Peer Reviewer for the study as well as to provide comment on the emission factors developed. The peer review addresses the assumptions and limitations made in the study. Appendix I contains AMEC's peer review report. Below are excerpts from the report.

6.1 Experimental Design Observations

During the development of the Experimental Design there was some discussion among the working group as to the applicability of the test method being used. The main point discussed being whether the method would benefit from the addition of an impinger prior to the treated filter. The theory was that if the HDI concentration and particle size distribution in the stack was large enough it could be possible that the treated filter would be overwhelmed and breakthrough could occur.

By way of an email communication on December 4th 2004, the following information was provided by the Bayer development team:

- During the development of the TDI method (III Report), break through studies using an impinger after the filter were performed and no TDI was found in the impinger.
- In the case of MDI, an impinger containing toluene was placed in front of a filter spiked with MDI-PP (Methylene Dianilinedi – Isocyanate, pyridylpiperazine derivative). This resulted in a loss of about 45% of the derivative.
- A break through study for HDI was performed in which an impinger was placed after the filter. The analyses showed no HDI in the impinger solution.
- Impingers, while generally effective for large particles, are less efficient for fine particulate (range of 0.5 – 1.5 microns). A review of the particle size data collected at each facility shows that approximately 95% of the particulate fall within this range.

Consequently, it was Bayer's opinion that adding an impinger to the train would simply be another source of error.

The experimental design initially included the measurement and/or recording of key parameters such as paint transfer efficiency; booth make-up air volumetric flow rate; and pressure drop across particulate control devices to allow for customizing of the emission factors for future site-specific conditions. After discussion amongst the working group, it was decided to remove the paint transfer efficiency calculations and pressure drop measurements across the particulate control devices from the program.

One of the operation scenarios proposed for the BASF site was to test emissions occurring when only a single part was in the booth. This scenario was later modified such that rather than a single part the entire car body would be present but only small sections (i.e. doors or rear panel) would be coated.

6.2 Source Testing Observations

No major deviations or items of concern were observed during the test periods. All sampling and recovery procedures were carried out as per the requirements of the test protocols.

There was a variation between the application procedures followed at the BASF and DuPont facilities. During the DuPont test program the mass of clear coat needed to complete the two (2) coats for the first test run of each Scenario was determined and then duplicated for the remaining two (2) tests of the Scenario. By following this procedure the mass of clear coat sprayed was identical for each of the three (3) tests for each Scenario. During the BASF testing, each coat of clear coat was applied as per normal operation and the mass of coating used for each test was determined. This resulted in a different mass of coating being used for each test of the program.

While the procedure used at DuPont would be expected to provide an additional level of control with respect to the concentrations determined for each scenario, the purpose of the study is to produce emission factors based on the mass collected versus mass sprayed. As such, the variation between the two (2) application procedures would not be expected to have a significant impact on the outcome of the study.

6.3 Uncertainty Analysis for Test Results

The uncertainty of a test result is based on the estimated accuracy of the raw measurements made (temperature, differential pressure, etc.) and the equations where the raw measurements are used.

In general, uncertainties associated with measurements can be divided into two (2) main classifications: Systematic and Random, also known as Determinant and Indeterminant. Calibration inaccuracy, reagent impurity and matrix interference, are all examples of systematic uncertainties. Random uncertainties are described by the laws of probability and are generally the results of inconsistencies in the standard operating procedures of sampling and analysis.

Contributions of systematic uncertainties to the overall uncertainty of the sampling program were not considered for the purposes of this study. Any systematic uncertainties due to improper calibration, faulty equipment, or inadequate test procedures would be in addition to the probable random uncertainty.

The California Air Resource Board (CARB) has documented a general procedure for determining the level of random uncertainty. Following this procedure, a basic percent uncertainty of the concentrations of HDI for each scenario was calculated. The results are presented in Table 10.

Table 10: General Uncertainty of HDI Concentrations

Facility	Concentration Percent Uncertainty (%)
DuPont Canada Inc., Ajax, On - Down Draft Booth	11.3% -11.8%
BASF, Toronto, On - Down Draft Booth	11.8%
BASF, Toronto, On -Semi Cross Draft Booth	10.9%
Ventra Plastics, Peterborough, On - Water Wash	11.2%/11.12%

From Table 10 we see that the range of uncertainty for the test program was between 10.9% and 11.8%. This range of uncertainty is considered standard for this type of test program. Two thirds (2/3) of the mass emission rate determinations should fall within this value if systematic errors are negligible.

6.4 Data Quality & Emission Factor Rating

The United States Environmental Protection Agency (US EPA) document, "Procedures for Preparing Emission Factor Documents; EPA-454/R-95-015, November 1997" was followed to determine a rating for both the data quality and emission factors. The data quality ratings are an assessment of the emissions data that will be used later to develop the emission factor. The emission factor rating is based on the ability of the overall average factor to represent a national annual average emission rate for the source category.

The test data collected was assigned a B rating due to the fact that while the testing was performed and reported in a way such that the information could be easily verified and duplicated, the test method used is a fairly new US EPA conditional test method rather than a reference method.

The emission factors developed from the data collected during the test programs were considered to be limited by the number of facilities tested and as a result were assigned a general C or D rating.

In conclusion, while the testing performed was limited by the number of facilities tested, the low variability in the emission factors returned from the DuPont and BASF facilities for the high solids coating would seem to support the validity of the test method used as well as the emission factors developed for this type of operation.

7.0 CONCLUSIONS

The objective of the study was to develop 1,6-hexamethylene diisocyanate emission factors for both the monomer and polyisocyanate forms, in grams of HDI emitted per kilogram of HDI sprayed for a variety of spray booth configurations and physical factors that are anticipated to have an effect on HDI emissions.

Emission factors have been developed for three (3) operating conditions as outlined in Table 11 below. Due to the limited number of tests performed during the study and the number of

physical factors that could affect the emissions no definitive conclusions can be made on the effect on HDI emissions by the following:

- Quality of filters;
- Age of filters;
- Size of paint job; and
- Transfer efficiency of the paint.

Table 11: Summary of HDI Emission Factors and Ratings (units: g HDI emitted/kg HDI sprayed)

Operating Conditions[1]	HDI Monomer Emission Factor[3]	HDI Polyisocyanate Emission Factor	Emission Factor Ratings[2]
Autobody Sector using Best Management Practices	**76**	**48**	**C**
Autobody Sector using Historical Practices	**81**	**63**	**C**
Original Equipment Manufacturer Sector	**35**	**18**	**D**

Table Notes:

(1) **Operating Conditions Definitions**

Autobody Sector using best management practices:

- Dry Filter Paint Booth (down draft or cross draft booths)
- High Efficiency Type Paint Spray System means equipment used for the application of automotive refinish coatings conforming to Section 3.4 *Application Equipment* of the Canadian Council of Ministers of the Environment (CCME) Guideline; "CCME Guideline" means the document entitled "National Standards and Guidelines for the Reduction of Volatile Organic Compounds from Canadian Commercial/Industrial Surface Coating Operations-Automotive Refinishing, October 1998, PN 1278", as amended, and published by the CCME;
- Approved Automotive Refinish Coatings means automotive refinish coatings that comply with the VOC content limits indicated in Section 3.2.1 *VOC Content Limits* of the National Standards; "National Standards" means the document entitled "National Standards for the Volatile Organic Compound Content of Canadian Commercial/Industrial Surface Coating Products Automotive Refinishing, October 1998, PN 1288" and published by the CCME;

Autobody Sector using historical practices:

- Dry Filter Paint Booth (down draft or cross draft booths);
- Old style Conventional Spray Systems;
- Unspecified Refinish Coatings.

Original Equipment Manufacturer Sector:

- Water Wash Paint Booth;
- Electrostatic Type Paint Spray System.

(2) Emission Factor Ratings Definitions

Ratings based on US EPA document "Procedure for Preparing Emission Factor Documents: EPA-454/R-95-015, November 1997"

C = Average. Emission factor is developed primarily from A, B and C rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.

D = Below Average. Emission factor is developed primarily from A, B and C- rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population.

(3) Limitations of Emission Factors

As mentioned above due to the limited nature of the study general emission factors have been developed for the three (3) operating conditions. The limited data of the study does not allow for any "customization" of the emission factors (i.e. accounting for differences in paint transfer efficiencies between the test condition and emission factor user's facility).

Auto body sector facilities with water wash paint booths should not use the emission factors derived for the original equipment manufacturer sector water wash booth as the operating conditions for the two (2) types of facilities are very different. As no testing was performed on auto body sector water wash booths it is recommended that auto body facilities with water wash booths use the auto body sector dry filter emission factors according to the paint and spray systems used.

Most MSDS provide a range of potential concentrations for isocyanates in each specific paint component and most regulators would require the highest potential concentration to be used to calculate emission estimates using these emission factors. However, it may be possible to obtain actual concentrations form paint manufacturers, enabling the user to reduce the resulting emission estimate, while also improving its accuracy.

8.0 RECOMMENDATIONS

It is recommended that should a future second stage of this study be considered that it would entail further testing to determine the effects on the HDI emissions by the following physical factors:

- Quality of filters;
- Age of filters;
- Size of paint job; and
- Transfer efficiency of the painting process.

This further data collection may allow for customization of the emission factors.